Chapter 4

Ion scattering data analysis methods

An inspection of the data acquired using low energy ion scattering techniques can be used to make qualitative statements on the crystalline structure under investigation, such as elemental identification and crystallographic symmetry directions. However, a quantitative description of the atomic structure and elemental composition of the surface region can only be obtained via a comparison with data generated using computational simulation methods [105]. This is the only viable option for including accurate ion-atom interaction potentials, lattice vibrations, multiple scattering and other effects in the analysis of low energy ion scattering data. Several approaches have been adopted in recent years and the most successful methods are discussed briefly in this chapter.

Many low energy ion scattering simulation programs have been developed by the adaptation of packages initially devised for analysis of medium energy ion scattering (MEIS) or Rutherford backscattering (RBS) experiments and allow different trial structures to be simulated for comparison with the experimental data. Broadly speaking, the various simulation packages fall under three distinct banners - Monte Carlo simulations, molecular dynamics simulations and hitting probability calculations. The basis of each of the three methods will be discussed, before focussing on the FAN package developed by Horst Niehus *et al.* [106] which has been specifically designed for low energy ion backscattering techniques, such as CAICISS, where the scattering angle is approximately 179°.

4.1 Monte Carlo ion scattering simulations

Monte Carlo simulations provide an opportunity to obtain information from systems which contain a large number of individual processes that can be described theoretically, but the combined effect of which cannot be described analytically. Monte

Carlo ion scattering simulations, such as MARLOWE, allow the complete trajectory of the scattered particle to be followed from its origin at the 'source', through the scattering event, to its detection at the 'detector' [107]. However, using such an approach yields a large number of trajectories where the ion is scattered through angles which do not then reach the detector and are therefore irrelevant to the analysis of the experimental data. This results in the need for large amounts of computation in order to generate a statistically favourable simulation of the experimental data. Obviously, this situation is undesirable and has led to the development of more efficient algorithms, such as the package developed by Goodstein and co-workers [108] which only follows trajectories which end in the vicinity of the detector. The main differences between the various MARLOWE packages arise from the different ways in which the algorithms treat the scattering event and the tracing out of the next collision partner in the scattering sequence [87]. A single-scattering approach is used, something which only holds true when the impact parameters which lead to significant deflection of the incident ion are low with respect to the crystal lattice dimensions [87]. Therefore, MARLOWE is much more suited to techniques using higher incident ion energies as problems may arise during the analysis of data in the low energy ion scattering regime.

In general, Monte Carlo methods have proved to be reasonably successful at simulating effects in the low energy regime when dealing with forward scattering techniques. These methods include not only the MARLOWE code [107] but also a range of other programs which are currently available, such as SABRE (dedicated to surface scattering only) [109], ACOCT [110], MATCH [111] and SARIC [112]. However, these packages are generally not best suited to the analysis of data acquired using a 180° backscattering geometry due to the large number of irrelevant ion trajectories which are simulated.

4.2 Molecular dynamic ion scattering simulations

In the molecular dynamics approach, the motion of a given number of particles are calculated over a certain period of time, with the motion governed by an interatomic pair-wise potential. When integrated over time, the calculations give a description of

the motion of the ion through the surface region [105]. This approach has been used to study a wide range of phenomena, such as thin film growth, protein structures and radiation damage of solids, but can also be applied to ion scattering [105]. Generally, the molecular dynamics approach focusses on the study of the trajectory of the ion and the scattering process at the surface [113]. However, due to the calculation of the motion of all the particles in the surface region during the scattering event, molecular dynamic simulations are significantly more time consuming than the Monte Carlo methods and are not widely applied to low energy ion scattering techniques.

4.3 Hitting probability packages

A third class of ion scattering simulation replicates the experimental data via the calculation of hitting probabilities. Tromp *et al.* [114] used this approach to develop the VEGAS code for the analysis of MEIS spectra, prior to an adaptation for low energy ion backscattering techniques by Daley *et al.* [115]. In a two-atom model, the probability of the incident ion hitting the target atom is calculated, prior to a calculation of the probability of the same ion being detected at a given detector position [114,116]. This approach incorporates lattice vibrations using a Gaussian distribution of displacements from the equilibrium position of the second atom. The hitting probabilities for all orientations are then summed up to give the intensity distribution as a function of the angle of incidence. In this approach, all of the simulated scattering events contribute to the final spectrum, saving vast amounts of computational time in comparison to both the Monte Carlo and molecular dynamics methods.

The hitting probability approach also has one drawback specific to low energy ion scattering applications in that multiple scattering can only be considered as a collection of uncorrelated events, and therefore cannot be included in the calculation. Hence, the hitting probability approach can only be applied when the chances of multiple scattering are low. For this, the shadow cone radius must also be small and therefore this simulation method is generally limited to the higher incident ion energies used in MEIS and RBS [114, 116].

4.4 The FAN simulation program and CAICISS data analysis

The FAN simulation program, an alternative approach to the simulation of low energy ion scattering spectra, specifically designed for backscattering applications, was developed by Horst Niehus and co-workers in Berlin [106, 117]. The Monte Carlo approach is not employed in this case. Instead, the trajectories always begin at the scattering centers, with the incident trajectories calculated by tracing out a "fan" of emission angles at the primary ion energy, E_0, such as is shown in figure 4.1. The outgoing trajectories are then calculated using the scattered particle energy, E_1, which is in turn determined by the experimental scattering angle. These procedures are similar to blocking cone calculations where the scattered intensity is calculated as a function of angle, taking into account the impact parameter, the ion-atom interaction potential and the scattering cross-section which were discussed in chapter 3. The two sets of 3D trajectory fans are calculated for all of the atoms in the specified structure, with a final angular scattering profile obtained by the multiplication of the incident and outgoing intensities. Given that both the incident and outgoing trajectories are calculated from within the crystal, only trajectories which will reach the detector are calculated, saving time compared to the other simulation approaches outlined previously. The FAN program has several useful features for the analysis of CAICISS data:

- Intensity profiles as a function of both polar angle and azimuthal angle.
- Up to three different atomic species in the trial structure.
- Choice of ion-atom interaction potential - ZBL or Molière and the screening correction factor in the Molière case.
- Includes effects due to sample temperature, neutralization and off-axis scattering.
- Atomic coordinates tuneable to $\pm$ 0.001 Å.

The program, however, does not include effects due to inelastic energy losses along the incident trajectory, which may slightly affect the radius of the shadow cones. To

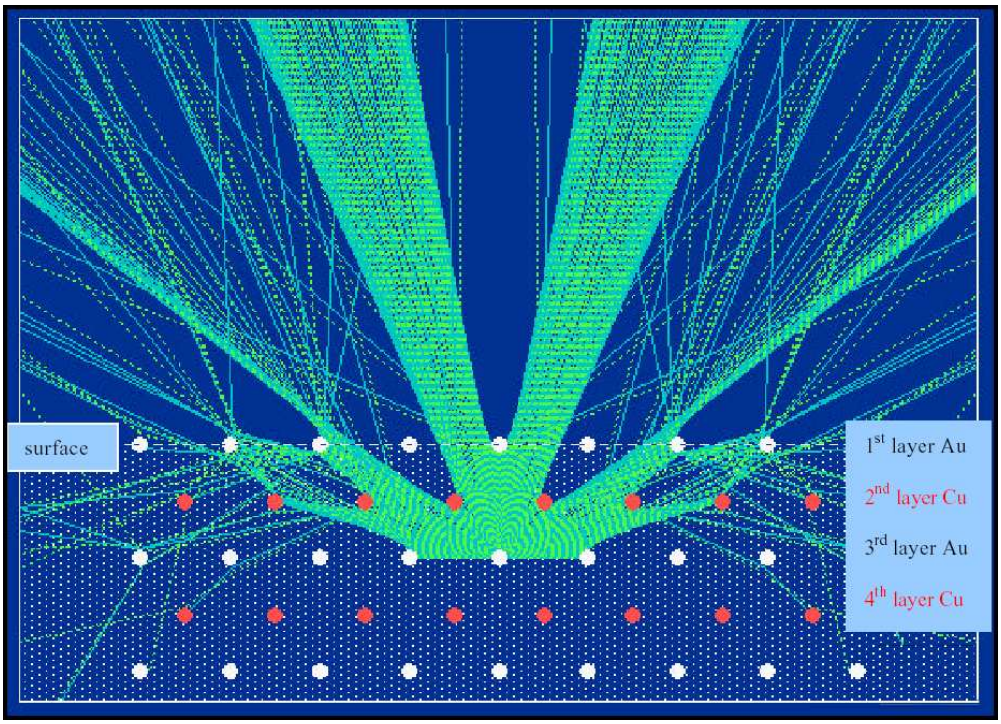

Figure 4.1: An illustration of the fan of particle trajectories which form the basis of the FAN simulation code. This example, from the FAN simulation guide [117], shows the trajectory fan calculated from a Cu atom in the third layer of a Cu-Au alloy structure. Trajectory fans for incident and outgoing particles are generated, originating at the scattering centers, which are then multiplied together to give the final intensity vs polar or azimuthal angle plot for comparison with the experimental data. The FAN simulation program is available from http://asp2.physik.hu-berlin.de/main.html.

date (February 2006), the package is limited to 1500 lattice points, making the simulation of more complex structures (e.g. quasicrystals) rather problematic. However, the current version of FAN has proven to be sufficient for the relatively simple structures detailed in the experimental chapters of this thesis. As will be demonstrated, the FAN software can be used to deduce a highly accurate model of the surface region, both in terms of atomic structure and chemical composition.

4.4.1 Extraction of CAICISS data for comparison with FAN simulations

In order to make a direct comparison between the experimental data and the output from the FAN simulation program, intensity profiles as a function of the polar

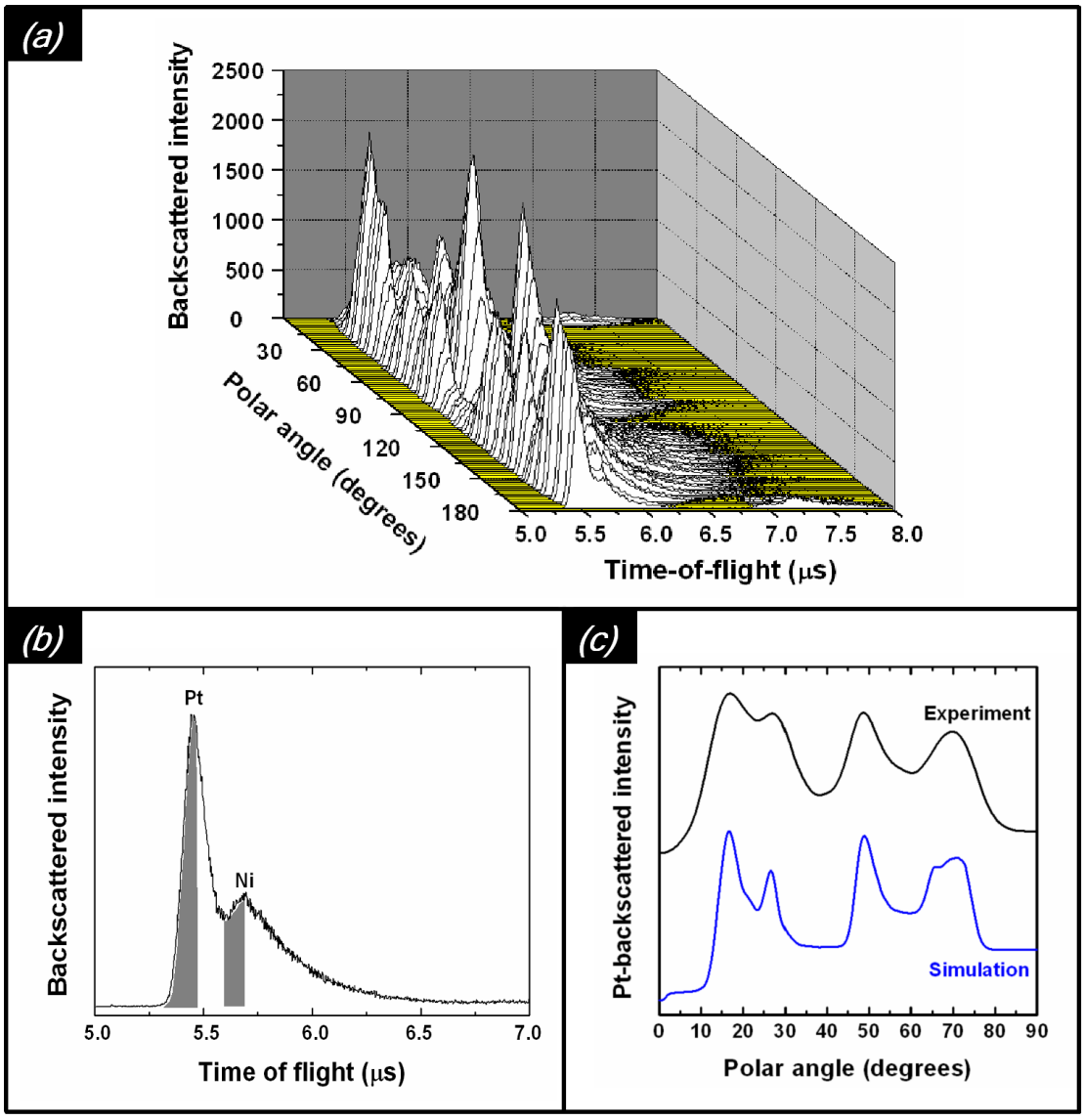

Figure 4.2: Example data from experiments involving Pt deposition on the Ni(110) surface. (a) shows the raw data with backscattered intensity plotted as a function of both time-of-flight and polar angle. (b) shows a single intensity vs time-of-flight spectrum from the data set, with the Pt peak at 5.47 μs and the Ni peak at 5.67 μs. The backscattered intensity from the peak, back to the background intensity on the low ToF side (the shaded area), is calculated for each element at each polar angle, yielding a polar angle plot for each element for comparison with the results of the corresponding FAN simulations, as shown in (c).

angle must be extracted from the CAICISS data. Figure 4.2(a) shows the raw data collected during the CAICISS experiment, in this case following Pt deposition on the Ni(110) surface, with intensity as a function of time-of-flight (ToF) measured at 1.8° polar angle intervals, as discussed in chapter 3. Figure 4.2(b) shows an individual intensity vs ToF plot acquired during the experiment. This plot is used to determine the ToF corresponding to the peak backscattered intensity from the Pt atoms (at 5.47 μs) and the Ni atoms (at 5.67 μs) in the surface region of the sample. The particles detected at shorter flight times (the shaded areas in figure 4.2(b)) give an indication of the energy resolution of the experiment. The total detected intensities from backscattering from Pt and Ni atoms is then calculated for each polar angle step in order to produce an intensity vs polar angle plot for each element in the sample. These plots can then be directly compared with the results of the FAN simulations (figure 4.2(c)) in order to obtain a more quantitative understanding of the atomic structure and chemical composition of the surface region.

Whilst informative about the elemental composition of the surface region, at this point the comparison of the FAN simulations with the intensity as a function of ToF plots obtained from the CAICISS experiment remains rather qualitative. Currently, the intensities of the two profiles are normalised using a high intensity feature (usually the surface peak), with the trial structure adjusted in order to fit all of the features in the spectrum, both in terms of intensity and polar angle. Many other ion scattering methods, and indeed many other surface science techniques, incorporate R-factor minimization into the analysis of the data [5, 118–122]. However, this method of comparison of the simulation results to the experimental data is not currently employed for the analysis of CAICISS data at Warwick. However, the current analysis methods do produce acceptable results, with typical errors of $\sim$ 1-2% in both the composition and changes to the atomic structure of the surface region.

In summary, the FAN software appears to be much better suited to the analysis of CAICISS data than any of the other available techniques. Whilst some issues within the quantitative analysis of the data need to be addressed, the FAN software provides sufficient accuracy for the analysis of the experiments discussed in this thesis.